

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
22 May 2003 (22.05.2003)

PCT

(10) International Publication Number
WO 03/042141 A1

(51) International Patent Classification⁷: **C07C 29/09**,
68/06, 31/20, B01J 21/10, 21/16, C07C 69/96

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(21) International Application Number: PCT/EP02/12640

(22) International Filing Date:
12 November 2002 (12.11.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
01309560.9 13 November 2001 (13.11.2001) EP

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VN, YU, ZA, ZM, ZW.

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(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK,
TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG).

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Published:

— with international search report

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*



WO 03/042141 A1

(54) Title: METHOD FOR THE CATALYTIC CONVERSION OF ALKYLENE CARBONATE WITH A MG, AL MIXED
(HYDR) OXIDE CATALYST

(57) Abstract: Method for catalytic conversion of alkylene carbonate, wherein alkylene carbonate is contacted with C₁-C₃ aliphatic
alcohol and/or water in the presence of Mg, Al mixed (hydr) oxide catalyst having a Mg: Al molar ratio in the range of from 4 to 20.

METHOD FOR THE CATALYTIC CONVERSION OF ALKYLENE CARBONATE WITH A MG,AL MIXED (HYDR) OXIDE CATALYST

The present invention relates to a method for catalytic conversion of alkylene carbonate, using an Mg, Al mixed (hydr)oxide catalyst, and a catalyst therefore.

5 EP-A-0 51 351 discloses an Mg, Al mixed (hydr)oxide catalyst having an Mg:Al molar ratio above 3 and preferably in the range from 3-10.

10 The article of H. Schaper et al. in Applied Catalysis, 54, (1989) 79-90, discloses the same catalyst. This catalyst has a hydrotalcite structure, consisting of brucite type layers in which part of the bivalent ions (Mg) are replaced by trivalent ions, alternated by interlayers which contain water and anions to compensate for the excess charge of the trivalent ions. The preparation of such catalysts is disclosed. Due to the
15 basic properties such catalysts are considered of special interest for base-catalyzed reactions, such as polymerisation of propylene oxide, double-bond isomerisations of olefins such as 1-pentene, and aldol condensations. Exemplified is double-bond isomerisation of 1-pentene
20 using an Mg, Al mixed oxide catalyst having an Mg:Al molar ratio of 5 and 10. At increasing molar ratio the conversion rate decreases.

25 The article of Watanabe, Y. et al. in Microporous and Mesoporous Materials 22 (1998) 399-407, discloses the use of Mg-Al hydrotalcite catalysts having a molar ratio of 1.8-2.5 for the methanolysis of ethylene carbonate for the production of dimethyl carbonate.

EP-A-0,478,073 describes a process for preparing a dialkyl carbonate which comprises contacting an alkylene carbonate with an alkanol in the presence of a mixed metal oxide catalyst or a modified bimetallic or polymetallic catalyst under conditions effective to produce the dialkyl carbonate. In the examples, a magnesium/aluminium mixed metal oxide catalyst having a Mg:Al ratio of 3:1 was employed.

In JP-A-06/238165, a process is described wherein an alkylene carbonate and an alcohol are subjected to transesterification in presence of a catalyst to produce a dialkyl carbonate. A combination of Magnesium oxide and another metal oxide other than magnesium was used as catalyst in an atomic ratio in the range of 1000:1 to 20:1 of magnesium to the other metal.

The present invention has for its object to provide a method for the catalytic conversion of alkylene carbonate having an improved conversion rate and improved yield, while having limited leaching of metal from the catalyst.

Accordingly, the invention provides a method for catalytic conversion of alkylene carbonate, wherein alkylene carbonate is contacted with C₁-C₅ aliphatic alcohol and/or water in the presence of Mg, Al mixed oxide catalyst having an Mg:Al molar ratio in the range of from 4 to 20.

The invention is based on the insight that by increasing the Mg:Al molar ratio in this type of (hydrotalcite) catalyst conversion rate and yield both improve. Although in the preparation of the catalyst a so called mixed Mg/Al hydroxide is formed it might be that under working conditions mixed Mg/Al oxides also or only are present. The catalyst will be referred to as Mg, Al (hydr)oxide catalyst. At molar ratios above 4, such as of

from 4 to 20 Mg:Al and, preferably, above 5 such as 5 to 20 the catalyst exhibits the highest activity.

During the catalytic conversion of alkylene carbonate metal oxide, in particular Mg, may leach from the catalyst particles. The leach rate is reduced when the Mg:Al molar ratio is below 20, such as of from 4 to 20, preferably below 10, such as of from 4 to 10. The Mg,Al (hydr)oxide catalyst suitable for the purpose of the present invention will therefore have a Mg:Al ratio of at least 4, preferably more than 4, even more preferably at least 5, and most preferably more than 5. The Mg,Al (hydr)oxide catalyst will further preferably have a Mg:Al ratio of at most 20, more preferably of less than 20, even more preferably of at most 15, again more preferably of less than 15, most preferably of at most 10.

Alkylene carbonate suitable for use in the catalytic conversion method according to the invention may be a C₁-C₅ alkylene carbonate such as 1,2 and 1,3 propylene carbonate, 1,2 and 2,3 butadiene carbonate. Preferred are ethylene carbonate and propylene carbonate. C₁-C₅ aliphatic alcohol suitable for use comprises a straight and branched C₁-C₅ alkanols. Preferred are methanol and ethanol. Most preferred is methanol. In the presence of one or a mixture C₁-C₅ alkanol the alcoholysis results in the formation of di(C₁-C₅)alkyl carbonate and alkylene diol. In the presence of only methanol the methanolysis results in the formation of dimethyl carbonate and the alkylene diol. The catalytic conversion in the presence of only water results by hydrolysis in the production of the alkylene diol and carbon dioxide. The catalytic conversion in the presence of C₁-C₅ aliphatic alcohol and water results in the formation of all end products in ratio's dependent on the methanol:water molar ratio. When

the molar ratio of methanol:water is higher than 6, such as 10 to 20. The dimethyl carbonate:alkylene diol molar ratio is between 1 and 0.

Another aspect of the invention relates to the use of this catalyst as defined above for the catalyst conversion of alkylene carbonate with C₁-C₅ aliphatic alcohol and/or water, and in particular to the methanolysis and/or hydrolysis of alkylene carbonate.

The Mg, Al mixed (hydr)oxide catalyst has generally a Mg:Al molar ratio in the range of from 4 to 20. At higher molar ratio's leaching of the metal oxide, in particular Mg increases. For an optimal catalyst activity at low Mg leaching the Mg:Al molar ratio is in the range of from 4 to 20, in particular of from 5 to 10 or of from 10 to 20.

The method and use of the catalyst according to the invention will be further elucidated by reference to the following examples which are provided for illustrative purposes and to which the invention is not limited.

Example 1: Catalyst preparation

The Mg/Al samples were prepared by semi-batch coprecipitation at constant pH. Aqueous solutions of Mg(NO₃)₂·6H₂O (1 M) and Al₂(SO₄)₃·18H₂O (0.5 M) were prepared from demineralised water and mixed proportionally to the targeted Mg/Al molar ratio. The resulting solution was then added drop-wise to 600 ml of an aqueous solution of 25% NH₃ (pH=9) under constant stirring at 65 °C. The precipitating solution was kept at pH=9 by addition of 25% NH₃ solution. The slurry was then aged for 1 hour under continuous stirring and filtered. The resulting paste was washed with demineralised-water until the pH of the wash water became neutral and, finally, dried over night at 80 °C.

Example 2: Catalyst screening

The samples were evaluated in a unit equipped with 6 quartz reactors having an inner diameter of 3 mm. Catalyst charges of 0.15 gram (30-80 mesh size) were diluted with 0.45 gram of SiC (0.05 mm diameter) and loaded into the reactor, with a pre-bed of 0.45 gram SiC placed on top. The catalysts were dried in situ under N₂-flow at 120 °C for 1 hour. The reactors were then pressurised to 25-30 bar and the feed flow is started with a space velocity of WHSV= 5 gr/(gr.hr), together with a moderate N₂ flow of WHSV= 2 gr/(gr.hr). The liquid feed consisted of a PC:MeOH mixture of 1:4 molar ratio. After a stabilising period of 20 hours at 120 °C, the liquid products were condensed at 15 °C and 1 bar during a 24 hours run for off-line GC analysis. The moderate N₂ flow needed for pressure regulation and product transport stripped some of the light ends from the sample. Therefore mass balances were only made on propylene carbonate.

In the following examples, the conversion of methanol and yield of dimethyl carbonate (DMC) are based on the molar amounts of these compounds divided by the molar amount of methanol supplied times 100%. The conversion of PC to monopropyleneglycol (MPG) and/or methylpropanyl-carbonate (MPC in mol%) and the yield of MPG and/or MPC are based on the molar amount of recovered PC divided by the molar amount of PC supplied in the feed times 100%.

Table 1: performance of Mg/Al (hydr)oxides for methanolysis of propene carbonate (120 °C, total liquid WHSV = 5 g/g/h, a N₂ flow of WHSV of 2 g/g/h and 25 bar, catalyst calcined at 400 °C unless specified otherwise)

Catalyst	Conv. MeOH ^a	PC ^b	Yield DMC ^a	MPG ^b	light ends ^b	MPC ^b
1 Mg/Al ^c	8.9	12.4	1.7	6.4	0.3	5.9
2 Mg/Al	9.0	11.5	1.5	5.5	0.4	6.0
5 Mg/Al	15.1	21.1	3.8	15.4	0.3	5.7
10 Mg/Al	17.4	25.3	4.7	20.2	0.4	5.1
20 Mg/Al	26.0	35.8	8.3	34.1	0.1	1.6
50 Mg/Al	25.0	34.1	8.0	32.5	0.0	1.6
Mg (OH) ₂	6.6	8.6	1.8	7.0	0.0	1.6
Effect of calcinations						
5 Mg/Al calc. 400 °C	15.1	21.1	3.8	15.4	0.3	5.7
5 Mg/Al calc. 80 °C	16.6	23.4	4.35	18.2	0.4	5.1
10 Mg/Al calc. 400 °C	17.4	25.3	4.7	20.2	0.4	5.1
10 Mg/Al calc. 80 °C	15.7	21.0	4.0	15.9	0.3	5.1

^a dimethyl carbonate expressed in mole% based on methanol supplied in feed; ^b monopropylene glycol and methyl propanyl carbonate (MPC) expressed in mole% based on propylene carbonate (PC) supplied in feed;

^c xMg/Al implies a Mg:Al molar ratio of x.

According to table 1, the activity of the mixed Mg/Al (hydr)oxides increases with increasing Mg/Al ratio, exception made for the pure $\text{Mg}(\text{OH})_2$ which shows one of the lowest activity, possibly because of leaching indicated by the formation of a hazy liquid product.

Calcining the materials at 80 or 400 °C prior to loading into the reactor had little influence on their catalytic performance. This illustrated for 5 Mg/Al and 10 Mg/Al in table 1.

The 20 Mg/Al and 50 Mg/Al catalysts exhibit the highest activity, but degrade to some extent during the reaction such that the catalyst/SiC bed was very hard to remove from the reactor. By contrast, the other samples came out as free flowing particles. The $\text{Mg}(\text{OH})_2$ sample was also free-flowing, though the haziness of the liquid product suggests significant leaching during the reaction.

Similar results have been obtained when using ethylene carbonate (EC) instead of propylene carbonate. Under the same operating conditions as applied for the examples of table 1, except for the ethylene carbonate which now substitutes the propylene carbonate in the feed, the 5 Mg/Al catalyst converted EC to EG with 28 mole% yield based on EC supplied in feed and a DMC/EG molar ratio of 0.89.

Example 3: Catalyst stability/activity

In order to assess the stability of the various materials, samples of 0.1 g of each catalyst were immersed in 15 ml of a representative MeOH:PC:MPG mixture (3.46:0.88:0.24 molar ratio) for 20 hours at room temperature. Then 5 ml samples were taken from the top of the liquid and analysed with ICP-spectrometry. The magnesium content of these products increased with the

Mg/Al molar ratio starting at Mg/Al of ~10 (Table 2). It is concluded that the 5 Mg/Al and 10 Mg/Al catalysts offer the best compromise between activity and stability in the reaction medium.

Table 2: Magnesium content of an MeOH:PC:MPG mixture (3.46:0.88:0.24 molar ratio) after 20 hours immersion of various Mg/Al mixed hydroxide at room temperature.

Catalyst	Mg leaching [mg/kg]
1 Mg/Al	9.30
2 Mg/Al	3.52
5 Mg/Al	10.14
10 Mg/Al	25.0
20 Mg/Al	34.5
50 Mg/Al	72.9
Mg	164.4

5 Example 4: Performance in methanolysis/hydrolysis:

10 The catalytic tests were carried out in a single-tube microflow unit which is equipped with a HPLC pump to feed the PC-MeOH-water mixture, a gas manifold to introduce N₂ at 0.7 Nl/h, a traced feed line, a stainless steel reactor of 15 mm ID (with thermowell) operating in down flow, a high-pressure condenser operating at room temperature and an automatic sampling manifold that distributes the liquid product sequentially over six bottle of 300 ml.

15 The reactor was typically charged with 2 g of catalyst (1.6 mm cylinders) diluted in 15 g of SiC. Once loaded, the reactor was heated up to reaction temperature (120-140 °C) under a N₂ flow of 0.7 Nl/h (i.e. WHSV of ~0.4 g N₂/g cat/h) at 25-30 bar for 16 h. The reactor was

then set to reaction temperature and pressure (25 bar),
contacted with the partially vaporised feed at target
velocity (typically 2 g liq./g cat/h) and operated under
varying conditions for more than 1000 hours without
interruption.

5

The liquid product was analysed off-line by means of
GC using the polar column. The gas stream was not
analysed. However, occasional use of a cold trap (-60 °C)
in the gas line did not provide more than 0.05 C% (based
on total feed) of additional product, which appeared to
be mainly methanol upon immediate GC analysis.

10

Table 3: performance of 5 Mg/Al (hydr)oxide for methanolysis and/or hydrolysis of propene carbonate (140 °C, total liquid WHSV = 2 g/g/h, a N₂ flow of WHSV of 0.4 g/g/h and 25 bar)

Feed MeOH:H ₂ O: PC	Conv. MeOH ^a	PC ^b	Yield DMC ^a	MPG ^b	light ends ^b	MPC ^b	DMC: MPG ^c
4:0:1	22.6	39.7	8.7	34.1	0.7	2.3	1.0
1:0:1	22.8	11.6	10.6	10.0	0.3	1.4	1.1
0.5:0:1	28.1	6.3	12.6	5.4	0.3	0.6	1.1
4:0:1	22.6	39.7	8.2	34.1	0.7	2.3	1.0
3.8:0.2:1	7.4	36.3	3.5	35.0	0.1	1.3	0.4
3.4:0.6:1	1.4	52.2	0.5	50.8	0.0	1.4	0.0
0.5:0:1	28.1	6.3	12.6	5.4	0.3	0.6	1.1
0.3:0.2:1	2.4	21.1	0.5	20.6	0.0	0.4	0.0
0:0.36:1	-	35.1	-	35.1	0.0	0.0	0.0

^a expressed in mole% based on methanol supplied in feed;

^b expressed in mole% based on PC supplied in feed;

^c expressed in mole:mole.

Table 3 shows that the 5 Mg/Al catalyst converts PC to MPG in the presence of methanol and/or water in varying ratio. The catalyst was stable for more than 1000 h and operated satisfactorily over a wide temperature range, from 120 to 180 °C and a variety of residence time, from 4 to 40 min (1/WHSV). By varying the feed composition it produced DMC/MPG in a ratio that varied from nearly 1:1 with a water-free feed to 0:1 with a methanol-free feed. The hydrolysis reaction turns out to proceed at higher rate than the methanolysis reaction

(compare e.g. the feed of 0:0.36:1 with 0.5:0:1, respectively). In contrast to the hydrolysis reaction, the methanolysis is limited by thermodynamic equilibrium. These two phenomena result in a DMC:MPG molar ratio in the product that drops much faster than do the MeOH:H₂O molar ratio in the feed. In other words, it suffices to substitute as small fraction of water for MeOH to uncouple the production of DMC from that of MPG.

The spent catalyst did not significantly differ from the fresh catalyst as characterised by XRD, XPS and bulk element analysis. The absence of significant chemical changes of 5 Mg/Al catalyst during the reaction of PC with MeOH is consistent with the low Mg and Al content (<10 ppm) of the liquid product measured by means of ICP analysis. When normalised to the production rate of MPG, the Mg leaching rate generally remained below 100 ppm (i.e. <100 mg Mg/kg MPG) and more typically <50 ppm. This low leaching rate holds for MeOH:PC as well as H₂O:PC and MeOH:H₂O:PC feeds.

Similar results are obtainable with other alkylene carbonates and C₂-C₅ aliphatic alcohols.

C L A I M S

1. Method for catalytic conversion of alkylene carbonate, wherein alkylene carbonate is contacted with C₁-C₅ aliphatic alcohol and/or water in the presence of Mg, Al mixed (hydr)oxide catalyst having a Mg:Al molar ratio in the range of from 4 to 20.
2. Method as claimed in claim 1, wherein the C₁-C₅ aliphatic alcohol is methanol or ethanol.
3. Method as claimed in claim 1 or 2, wherein the Mg:Al molar ratio is above 4.
4. Method as claimed in claim 1 to 3, wherein the alkylene carbonate is ethylene carbonate or propylene carbonate.
5. Method as claimed in claim 1 to 4, wherein the molar ratio of methanol:water is below 20, preferably below 10.
6. Use of a catalyst as defined in claims 1 to 3 for the catalytic conversion of alkylene carbonate with C₁-C₅ aliphatic alcohol and/or water.
7. Use of a catalyst of claim 6 for the alcoholysis and/or hydrolysis of alkylene carbonate.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/12640

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C29/09 C07C68/06 C07C31/20 B01J21/10 B01J21/16
C07C69/96

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, EPO-Internal, BEILSTEIN Data, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 478 073 A (UNION CARBIDE CHEM PLASTIC) 1 April 1992 (1992-04-01) cited in the application page 4, line 22 - line 24 page 5, line 16 - line 19 page 8, line 12 - line 13 page 8, line 41 - line 43 page 9, line 11 - line 18 page 14 -page 17; examples 3,4,7-18; tables I,II --- -/--	1-7

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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8 document member of the same patent family

Date of the actual completion of the international search

20 February 2003

Date of mailing of the international search report

28/02/2003

Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/12640

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	T. TATSUMI ET AL.: "Hydrotalcite-type materials as catalysts for the synthesis of dimethyl carbonate from ethylene carbonate and methanol" MICROPOROUS AND MESOPOROUS MATERIALS., vol. 22, 1998, pages 399-407, XP002196014 ELSEVIER SCIENCE PUBLISHING, NEW YORK., US ISSN: 1387-1811 cited in the application page 405; table 3 page 405, right-hand column, paragraph 2 ----	1,6
A	EP 0 893 428 A (NIPPON CATALYTIC CHEM IND) 27 January 1999 (1999-01-27) page 6; table 1 comparative example 1 ----	1,6
A	PATENT ABSTRACTS OF JAPAN vol. 018, no. 619 (C-1278), 25 November 1994 (1994-11-25) & JP 06 238165 A (NIPPON SHOKUBAI CO LTD), 30 August 1994 (1994-08-30) abstract ----	1,6
A	EP 0 478 075 A (UNION CARBIDE CHEM PLASTIC) 1 April 1992 (1992-04-01) examples 1,4,5,7,12 ----	1,6
A	US 4 691 041 A (DURANLEAU ROGER G ET AL) 1 September 1987 (1987-09-01) the whole document ----	1
A	H. SCHAPER ET AL.: "Stabilized Magnesia: a Novel Catalyst (Support) Material" APPLIED CATALYSIS, vol. 54, 1989, pages 79-90, XP008002450 AMSTERDAM, NL ISSN: 0166-9834 cited in the application the whole document -----	1,6

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/12640

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0478073	A	01-04-1992	CA 2051488 A1 EP 0478073 A2 JP 6025103 A MX 9101179 A1	21-03-1992 01-04-1992 01-02-1994 04-05-1992
EP 0893428	A	27-01-1999	JP 2631803 B2 JP 6211751 A EP 0893428 A1 DE 69324331 D1 DE 69324331 T2 EP 0599287 A1 KR 192771 B1 US 5430170 A	16-07-1997 02-08-1994 27-01-1999 12-05-1999 02-09-1999 01-06-1994 15-06-1999 04-07-1995
JP 06238165	A	30-08-1994	NONE	
EP 0478075	A	01-04-1992	US 5164497 A AT 173242 T AU 8464391 A CA 2051484 A1 DE 69130474 D1 DE 69130474 T2 DK 478075 T3 EP 0478075 A2 ES 2123504 T3 JP 2889975 B2 JP 4279540 A KR 180242 B1 MX 9101188 A1	17-11-1992 15-11-1998 02-04-1992 21-03-1992 17-12-1998 27-05-1999 03-05-1999 01-04-1992 16-01-1999 10-05-1999 05-10-1992 15-05-1999 04-05-1992
US 4691041	A	01-09-1987	EP 0298167 A1 JP 1031737 A DE 3781796 D1 DE 3781796 T2	11-01-1989 02-02-1989 22-10-1992 11-02-1993

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